3843-55-8; **17b**, 112740-31-5; **18**, 88792-61-4; **19**, 88792-64-7; **21**, 112740-32-6; **22**, 109273-93-0; **23**, 84810-71-9; **24**, 112740-37-1; **25**, 112740-38-2; **26**, 112740-39-3; **27**, 84810-72-0; **27′**, 109273-94-1; **28**, 112740-40-6; **29**, 112763-18-5; **30**, 77219-86-4; **31**, 112740-41-7; **32**, 112740-42-8; **33**, 112740-43-9; **34**, 112740-46-2; 1,5-dimethoxy-3-[2-(phenylseleno)propionyl]-4-naphthol, 88792-63-6; 2-(methoxymethyl)-1,4-pentadiene, 57217-20-6; [(*Z*)-4-(methoxymethyl)-2,4-pentadienyl]trimethyltin, 112740-34-8.

Furan-2-carbaldehyde Dimethylhydrazones in Diels–Alder Cycloadditions[1]

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Received March 5, 1987

Furan-2-carbaldehyde dimethylhydrazone and maleic anhydride and N-substituted maleimides and fumaronitrile in chloroform at room temperature readily formed nonisolable 1:1 cycloadducts which spontaneously lost water, giving 1,2,3-trisubstituted benzenes in good yield. With alkynic dienophiles no cycloaddition occurred, and with quinones Michael addition of the furan nucleus to the quinone was the preferred reaction.

1,4-Cycloadditions of furans with alkenic and alkynic dienophiles provide convenient entry to a variety of 7-oxabicyclo[2.2.1]heptanes and -heptenes,[2] which, by opening of the oxygen bridge, offer a convenient route to unusually substituted benzenes. Cycloadditions of substituted thiophenes[3] and *N*-aminopyrrole derivatives[4] are also useful methods for obtaining substituted benzenes as well as for the annulation of benzene rings. Vinyl derivatives of these five-membered heterocycles, however, also undergo cycloaddition under a variety of reaction conditions except that in these instances the diene is comprised of the exocyclic vinyl group and the endocyclic double bond of the heterocyclic ring. Such cycloadditions result in benzo[*b*]furans,[5a] benzo[*b*]thiophenes,[5b] and benzo[*b*]pyrroles[5c] when electron-deficient dienophiles are used.

Furfural and related furans substituted with electron-withdrawing groups are poor dienes in these types of cycloadditions, restricting entry to arenes containing 1,2,3 arrangements of electron-withdrawing groups. As these initial furan substituents are meta-directing groups in benzene substitution, more circuitous routes are needed for the synthesis of these arenes. Recent work in which methacrolein dimethylhydrazone functioned[6] as a 1-azadiene leading to pyridine derivatives suggested that incorporation of the dimethylhydrazono group into furan and related five-membered heterocycles would have the potential for enhancing the dienic character of the ring system. MO calculations[7] show that by introducing the dimethylhydrazono group into the furan nucleus an increase in its HOMO energy, relative to that of furan and 2-vinylfuran, results. A significant increase in the HOMO coefficient at the C-5 position compared to that at the C-2 position also occurs, consistent with an increase in electron density at that position due to resonance interaction with the hydrazono substituent (Figure 1).

Furfural dimethylhydrazone (**1a**), readily prepared[8] from furfural and *unsym*-dimethylhydrazine in refluxing benzene/catalytic amount of *p*-toluenesulfonic acid, reacted with maleic anhydride in $CHCl_3$ (room temperature, 16 h), giving 3-dimethylhydrazonophthalic anhydride (**3a**) in almost quantitative yield as bright yellow needles. Similarly, **1a** and *N*-ethylmaleimide resulted in **3b** (90%).

The reactions proceed by formation of an initial 1:1-cycloadduct **2** derived from the dienic system of the furan ring and the dienophile. This initial cycloadduct cannot be isolated and undergoes aromatization by the spontaneous elimination of H_2O. We were not able to follow the development of the intermediate **2** using NMR techniques. This is analogous to the reported[9] aromatization of the adduct from maleic anhydride and the bis-anil formed from substituted furfural and *p*-phenylenediamines. In addition, the dehydration to the benzenoid system is aided by electron donation from the hydrazono substituent assisting in the rupture of the oxygen bridge. Cycloaddition occurring across the furan ring rather than across the vinyl system may also be due to the conformational preference of the furan aldehyde group,[10] which does not favor the cisoid azadiene form of the hydrazone.

These cycloadditions provide a convenient route to substituted benzenes such as 3-hydroxyphthalide-7-carboxylic acid (**4**). This was obtained by acid hydrolysis (15% aqueous HCl) of **3a** to give the formyl dicarboxylic acid which rearranged to **4**. Spectral data were consistent with the assigned structure **4**, especially ν_{OH} 3500–3160 cm^{-1}, ν_{CO} 1800–1610 cm^{-1}, and the presence of a benzylic hydrogen at δ 8.26. The phthalide **4** is of special interest

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[1] Abstracted from the Ph.D. Thesis of E.B.W., 1985.

[2] For recent reviews, see: Dean, F. M. *Adv. Heterocycl. Chem.* **1981**, *30*, 168.

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[7] Determined by simple Hückel calculations in which the ω technique was used to obtain self-consistency [Streitwieser, A. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961, p 115].

[8] The dimethylhydrazones could be prepared in a pure state and kept without decomposition at low temperatures. They were thoroughly characterized by spectral data as satisfactory analytical data were not obtained due to slight decomposition during transit.

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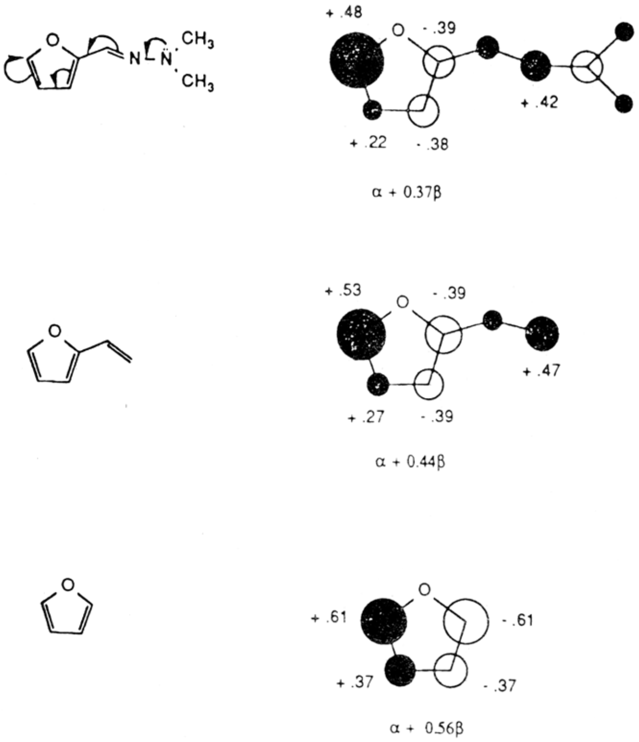
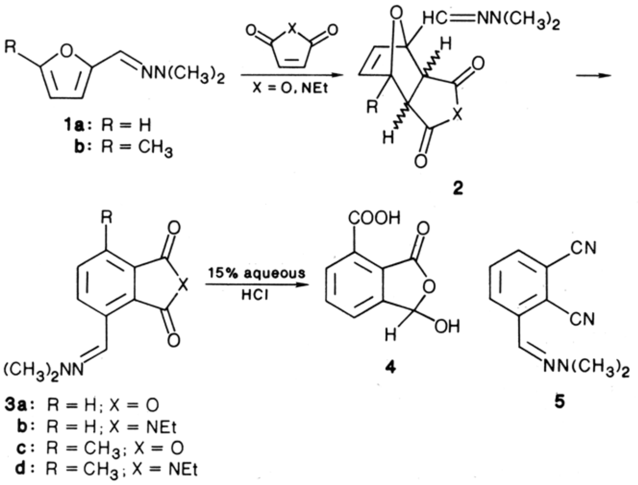


Figure 1. Coefficients of the HOMO of furfural dimethylhydrazone (**1a**), 2-vinylfuran, and furan.

for use in annelation reactions with quinone monoketals leading to anthraquinone systems.[11a]

Fumaronitrile also added to **1a** (R = H) to give **5**. However, cycloaddition required stannic chloride catalysis which reduced the yield to 13% due to extensive polymerization of the diene by the Lewis acid catalyst. Coordination of Lewis acids to diazo derivatives has been observed[11b] and was evident upon addition of $BF_3{\cdot}OEt_2$ to **1a** which resulted in the change from a colorless solution to a light purple solution.



1a: R = H
b: R = CH₃

2

3a: R = H; X = O
b: R = H; X = NEt
c: R = CH₃; X = O
d: R = CH₃; X = NEt

4

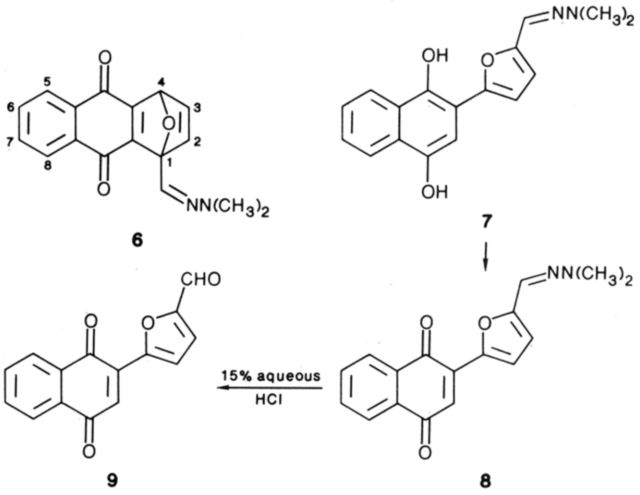
5

In contrast to the reaction of **1a**, thiophene-2-carbaldehyde dimethylhydrazone reacted with maleic anhydride (xylene, 16 h) to give **3a** and H_2S in only 6% yield. Cycloaddition of the thiophene or furan hydrazone with maleic acid did not occur; instead, ready protonation of the hydrazone in either ether or benzene resulted.

5-Methylfurfural dimethylhydrazone (**1b**) and maleic anhydride in chloroform (room temperature, 16 h) gave **3c** as bright orange prisms but in reduced yield (74%). Similarly **1b** and *N*-ethylmaleimide gave **3d** after purification by chromatography (silica gel, $CHCl_3$) as bright yellow needles, also in reduced yields (65%). The corresponding dimethylhydrazones from 5-nitrofurfural and 2-acetylfuran, on the other hand, failed to undergo cycloaddition with the above dienophiles under a variety of conditions.

Cycloaddition of **1a** with naphtho- and azanaphthoquinones has the potential for leading directly to anthraquinone derivatives with carbonyl substituents in the 5-position. However, the reaction of **1a** with 1,4-naphthoquinone in boiling toluene (2 h) or benzene (16 h) gave a 77% yield of a deep purple, oxidized 1:1 cycloadduct. Coupling in its ^1H NMR spectrum showed this product to be the oxidized Michael adduct **8** and not the cycloadduct **6**. If the oxidized Diels–Alder cycloadduct **6** were obtained, coupling between the C-1 and C-2 hydrogens and the C-3 and C-4 hydrogens would be observed. Similar coupling was reported by McCulloch and co-workers[12a] to be in the range of 1.6 Hz in furan–DMAD cycloadducts, and coupling of this order is absent in the ^1H NMR spectrum of our product. ^{13}C APT NMR spectroscopy was consistent with structure **8** with the presence of 2 × C═O, 4 × C, 8 × CH, and 2 × CH_3 groups; however, these data are also consistent[12b] with the cycloadduct **6**.

Hydrolysis of **8** with dilute aqueous HCl (2 h) resulted in the formation of the aldehyde **9** as golden-straw colored needles, confirming the structure of **8**. These results are in agreement with those of Bridson and co-workers[13] who found that furans and naphthoquinones undergo oxidative coupling in the presence of chloranil or other oxidizing agents; the in situ oxidation of the initial Michael product prevents a retro reaction from occurring. Others have also found[14] furans to be unreactive toward naphthoquinones not bearing electron-withdrawing groups. In the present instance, the hydrazono substituent increases the nucleophilicity of the 5-position of the furan nucleus, Michael addition occurring to **7** which undergoes aerial oxidation



6

7

9

8

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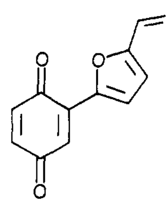
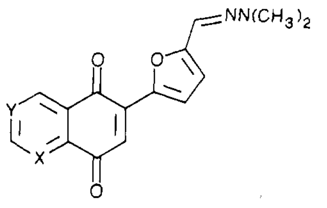
in the reaction mixture to **8**. When the furan **1a** was added to an ether solution of 1,4-naphthoquinone containing 2 equiv of $BF_3 \cdot OEt_2$ under an argon atmosphere (0 °C, 1 h), the naphthoquinol **7** was isolated since oxidation to the quinone was eliminated. The addition also occurred in the absence of BF_3, although in reduced yield.

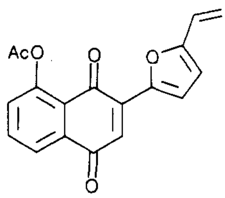
Similar reactions of the furfural hydrazone with benzoquinone, quinoline-5,8-dione, isoquinoline-5,8-dione, and 5-acetoxy-1,4-naphthoquinone gave the corresponding Michael adducts **8a**, **10a**, **10b**, and **11**. Structural assignments are based on the established regiochemistry of the quinones[15] with addition occurring β to the more electron-deficient carbonyl group. Reaction with 5-hydroxynaphthoquinone resulted in no product formation and decomposition of starting material.



8a



10a: X = N; Y = CH
b: X = CH; Y = N



11

Experimental Section[16]

Furfural Dimethylhydrazone (1a). A stirred solution of distilled furfural (30.0 g, 0.30 mol) in benzene (30 mL) containing a catalytic amount of TsOH (15 mg) was treated carefully with *N*,*N*-dimethylhydrazine (16 g, 0.30 mol), the exothermic reaction being cooled in an ice-bath. The solution was then refluxed for 4 h and the H_2O formed during the reaction was removed in a Dean–Stark trap. The solution was distilled through a Vigreux column, giving the diene as a colorless mobile oil: 32.2 g (74%), bp 69 °C/2 mm; ^1H NMR (200 MHz, $CDCl_3$) δ 7.39 (d, 1, $J_{4,3}$ = 1.62 Hz, H_4), 7.13 (s, 1, HC=N), 6.37 (d, 1, J = 2.93 Hz, H_2), 6.39 (dd, 1, $J_{3,4}$ = 1.62 Hz, $J_{3,2}$ = 2.93 Hz, H_3), 2.95 [s, 6, $N(CH_3)_2$].

5-Methylfurfural dimethylhydrazone (1b), prepared in the same manner from 5-methylfurfural, was obtained as a colorless oil which became pale yellow on storage: 29.0 g (83%), bp 55–60 °C/0.5 mm; ^1H NMR (200 MHz, $CDCl_3$) δ 7.10 (s, 1, *H*C=N), 6.25 (d, 1, $J_{2,3}$ = 3.14 Hz), 5.99 (d, 1, $J_{2,3}$ = 3.14 Hz), 2.93 [s, 6, $N(CH_3)_2$], 2.33 (s, 3, CH_3).

3-Dimethylhydrazonophthalic Anhydride (3a). Furfural dimethylhydrazone (2.0 g, 0.045 mol) and maleic anhydride (1.0 g, 0.0122 mol) were stirred at room temperature in dry $CHCl_3$ (30 mL). Upon addition of the diene a bright orange-red color developed. After 16 h the $CHCl_3$ solution was evaporated, and the residue was triturated with a small amount of anhydrous ether and was then collected. The cycloadduct was obtained as bright yellow needles: 2.5 g (94%) ($CHCl_3$), mp 173–174 °C. Compounds **3b** (90%, yellow needles from EtOH, mp 141–142 °C), **3c** (74%, bright orange prisms from EtOH, mp 135–136 °C), and **3d** (65%, bright yellow needles from EtOH, mp 145–146 °C) were prepared in this manner. All compounds had satisfactory analytical data (±0.4% C, H, N) and their spectral characteristics are described in ref 12b.

3-Dimethylhydrazonophthalic anhydride (3a) was also prepared from maleic anhydride (0.8 g, 0.008 mol) and thiophene-2-carbaldehyde dimethylhydrazone (1.8 g, 0.012 mol) in anhydrous xylene (30 mL) under reflux for 16 h. The reaction mixture was cooled and filtered, affording a small amount of insoluble material. The filtrate was evaporated, leaving a thick orange oil which was passed through a small silica gel column and eluted with $CHCl_3$. Evaporation of the $CHCl_3$ and trituration with ether gave the above anhydride **3a**, identical in all respects with that obtained in the reaction using furfural dimethylhydrazone: 0.1 g (6%).

3-Hydroxyphthalide-7-carboxylic Acid (4). Phthalic anhydride 3-dimethylhydrazone (2.9 g, 0.014 mol) was partially dissolved in 15% aqueous HCl (30 mL). The mixture was heated to 50 °C at which time the hydrazone completely dissolved and the solution become colorless. Heating was continued for 16 h. The solution was cooled to 10 °C and the hydroxyphthalide precipitated as colorless needles: 2.5 g (92%), mp 173–174 °C (H_2O) (lit.[17] mp 165.5–168.5 °C); IR (KBr) 3500–3160 (ν_{OH}) cm^{-1}, 1800–1610 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (200 MHz, DMSO-d_6) δ 8.26 (s, 1, H_3), 7.84 (br s, 3, Ar), 6.70 (s, 1 OH); MS, $M^{\cdot+}$ 194 (100).

Anal. Calcd for $C_9H_60_5$: C, 55.68; H, 3.12. Found: C, 55.67; H, 3.16.

1,2-Dicyano-3-dimethylhydrazonobenzene (5). A stirred solution of fumaronitrile (1.0 g, 0.0144 mol) in anhydrous benzene (50 mL) containing a catalytic amount of stannic chloride (2 mL) was treated with furfural dimethylhydrazone (2.1 g, 0.015 mol). The solution turned reddish brown immediately, the color changing to green as the reaction proceeded. After 5 h the mixture was poured into H_2O (100 mL) and the benzene removed. The aqueous layer was extracted with $CHCl_3$ (3 × 10 mL). The organic fractions were combined, washed sequentially with brine (100 mL) and H_2O (2 × 100 mL), dried (anhydrous Na_2SO_4), and evaporated to afford the dicyano compound which solidified on standing, forming long green needles from ethanol: 0.4 g, 13%, mp 165–166 °C.

Anal. Calcd for $C_{11}H_{10}N_4$: C, 66.65; H, 5.08; N, 28.27. Found: C, 66.61; H, 5.12; N, 28.26.

2-(5-Dimethylhydrazonofur-2-yl)naphthalene-1,4-diol (7). A solution for 1,4-naphthoquinone (2.0 g, 0.012 mol) and $BF_3 \cdot OEt_2$ (3.4 g, 0.024 mol) in anhydrous ether (100 mL) at 0 °C in an argon atmosphere was stirred for 30 min. Furfural dimethylhydrazone (2.0 g, 0.014 mol) was added and stirring continued for 2 h. The yellow-green reaction mixture was poured into H_2O (200 mL) and extracted with $CHCl_3$ (4 × 100 mL), the organic layer becoming dark purple in color. The organic fractions were combined, washed with H_2O (2 × 50 mL), dried (anhydrous Na_2SO_4), and evaporated. This afforded the diol **7** as blue irregular prisms: 3.0 g (84%), mp 136–140 °C; IR (KBr) 3650–3000 (ν_{OH}), 1580 ($\nu_{C=N}$) cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 8.35–8.10 (m, 2, Ar), 8.05–7.50 (m, 3, Ar), 7.40 (d, 1, $J_{2',3'}$ = 3.5 Hz, $H_{1'}$ or $H_{3'}$), 6.45 (d, 1, $J_{2,3}$ = 3.5 Hz, $H_{2'}$ or $H_{3'}$), 2.97 [s, 6, $N(CH_3)_2$]; MS, $M^{\cdot+}$ 296 (45).

2-(5-Dimethylhydrazonofur-2-yl)-1,4-naphthoquinone (8). 1,4-Naphthoquinone (5.0 g, 0.03 mol) and furfural dimethylhydrazone (5.0 g, 0.036 mol) in anhydrous toluene (200 mL) were refluxed for 2 h at which time TLC indicated the disappearance of starting material. The toluene was removed under reduced pressure and the resulting residue subjected to HPLC eluting with $CHCl_3$/hexane (1:1). This afforded the oxidized Michael adduct **8** as dark purple prisms: 6.8 g (77%), mp 175–176 °C (CH_2Cl_2/hexanes); IR (KBr) 1670 ($\nu_{C=O}$), 1650 ($\nu_{C=O}$), 1585 ($\nu_{C=N}$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.16–8.07 (m, 2, H_5 and H_8), 7.76–7.71 (m, 2, H_6 and H_7), 7.78 (d, 1, $J_{2',3'}$ = 3.8 Hz, $H_{3'}$), 7.35

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(16) Spectal characterizations were carried out on the following instruments: infrared spectra, Perkin-Elmer Model 298 or 337 grating infrared spectrophotometers; ^1H NMR spectra, Perkin-Elmer R600 or Varian XL-200 spectrometer with tetramethylsilane as an internal standard; ^{13}C NMR, Varian XL-200 spectrometer at 50.3 MHz with tetramethylsilane as an internal standard; mass spectra; the Hewlett-Packard GC-MS system Model 5987A. All melting points were determined in capillaries by using a Thomas-Hoover capillary melting point apparatus for samples melting below 200 °C or a Melt-Temp apparatus and are uncorrected. Evaporations were carried out under reduced pressure by using a Buchi Rotovap apparatus. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN, or Atlantic Microlab, Inc., Atlanta, GA.

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(s, 1, H_3), 7.05 (s, 1, *H*C=N), 6.61 (d, 1, $J_{2',3'}$ = 3.8 Hz, $H_{2'}$), 3.09 (s, 6, CH_3); ^{13}C NMR (200 MHz, $CDCl_3$) δ 184.65 (*C*=O), 183.25 (*C*=O), 156.10, 145.65, 134.73, 133.86, 133.29, 132.52, 132.43, 126.63, 126.25, 125.89, 121.93, 119.75, 109.65, 42.53 [$N(CH_3)_2$]; ^{13}C APT NMR ($CDCl_3$), 2 × C=O, 4 × C, 8 × CH and 2 × CH_3; MS, $M^{\bullet+}$ 294 (100).

Anal. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.39; H, 4.79; N, 9.52. Found: C, 69.18; H, 4.88; N, 9.26.

2-(5-Formylfur-2-yl)-1,4-naphthoquinone (9). 2-(5-Dimethylhydrazonofur-2-yl)-1,4-naphthoquinone (1.5 g, 0.005 mol) was refluxed for 2 h in a 15% aqueous HCl solution (50 mL). Stirring was then continued for 16 h at room temperature. The solution was poured into ice–H_2O (200 mL), precipitating a green solid which was filtered. The product was worked up by HPLC eluting with $CHCl_3$, followed by sublimation, affording the aldehyde as golden, straw-colored needles. Additional compound was obtained by neutralizing the aqueous fraction with $NaHCO_3$ and extracting with $CHCl_3$: 0.95 g (74%), mp 180–181 °C (EtOH); IR (KBr) 3400 (ν_{OH}), 2900 (ν_{CHO}, w), 1445 (ν_{CHO}, w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.79 (s, 1, C*H*O), 8.18–8.11 (m, 2, Ar), 7.83–7.76 (m, 2, Ar), 7.77 (d, 1, $J_{2',3'}$ = 3.8 Hz, $H_{3'}$), 7.60 (s, 1, H_3), 7.38 (d, 1, $J_{3',2'}$ = 3.8 Hz, $H_{2'}$); MS, $M^{\bullet+}$ 252 (100) [M + 1].

Anal. Calcd for $C_{15}H_8O_4$: C, 71.43; H, 3.20. Found: C, 71.27; H, 3.24.

2-(5-Dimethylhydrazonofur-2-yl)benzoquinone (8a). A solution of benzoquinone (2.0 g, 0.0185 mol) and furfural dimethylhydrazone (2.7 g, 0.019 mol) in anhydrous benzene (100 mL) was refluxed for 24 h. The benzene was removed under reduced pressure and the residue purified by column chromatography (silica gel/$CHCl_3$). Crystallization from CH_2Cl_2/hexane afforded the oxidized Michael adduct **8a** as bright purple rosettes: 3.8 g (84%), mp 126–127 °C; IR (KBr) 1658 ($\nu_{C=O}$), 1635 ($\nu_{C=O}$), 1580 ($\nu_{C=N}$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.51 (d, 1, $J_{2',3'}$ = 3.80 Hz, $H_{2'}$), 7.02 (s, 1, H_3), 6.80 (s, 2, H_4 and H_5), 6.73 (s, 1, *H*C=N), 6.53 (d, 1, $J_{2',3'}$ = 3.80 Hz, $H_{3'}$), 3.80 [s, 6, $N(CH_3)_2$], MS, $M^{\bullet+}$ 244 (100).

Anal. Calcd for $C_{13}H_{12}N_2O_3$: C, 63.92; H, 4.95; N, 11.47. Found: C, 63.96; H, 4.96; N, 11.46.

The following compounds were prepared in the same manner as 8 above.

6-(5-Dimethylhydrazonofur-2-yl)quinoline-5,8-dione (10a), obtained as bright purple needles from EtOAc (62%): mp 194–195 °C; IR (KBr) 1665 ($\nu_{C=O}$), 1640 ($\nu_{C=O}$), 1580 ($\nu_{C=N}$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.05 (dd, 1, $J_{2,3}$ = 4.69 Hz, $J_{2,4}$ = 1.69 Hz, H_2), 8.47 (dd, 1, $J_{4,3}$ = 7.86 Hz, $J_{4,2}$ = 1.69 Hz, H_4), 7.71–7.65 (m, 2, H_3 and $H_{4'}$ or $H_{3'}$), 7.51 (s, 1, H_7), 7.03 (s, 1, *H*C=N), 6.63 (d, 1, *J* = 3.88 Hz, $H_{4'}$ or $H_{3'}$, 3.11 [s, 6, $N(CH_3)_2$]; MS, $M^{\bullet+}$ 295 (100).

Anal. Calcd for $C_{16}H_{13}N_3O_3$: C, 65.07; H, 4.44; N, 14.23. Found: C, 64.99; H, 4.48; N, 14.21.

7-(5-Dimethylhydrazonofur-2-yl)isoquinoline-5,8-dione (10b) formed dark purple needles from EtOAc/hexane (59%): mp 186–188 °C; IR (KBr) 1665 ($\nu_{C=O}$), 1660 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 9.38 (s, 1, H_1), 9.05 (d, 1, $J_{3,4}$ = 5.01 Hz, H_3), 7.88 (d, 1, $J_{4,3}$ = 5.01 Hz, H_4), 7.75 (d, 1, $J_{3,4}$ = 5.01 Hz, H_3), 7.15 (d, 1, *J* = 3.74 Hz, $H_{4'}$ or $H_{3'}$), 7.34 (s, 1, H_6), 7.03 (s, 1, *H*C=N), 6.64 (d, 1, *J* = 3.74 Hz, $H_{4'}$ or $H_{3'}$), 3.14 [s, 6, $N(CH_3)_2$]; MS, $M^{\bullet+}$ 295 (100).

Anal. Calcd for $C_{16}H_{13}N_3O_3$: C, 65.07; H, 4.44; N, 14.23. Found: C, 65.15; H, 4.45; N, 14.23.

8-Acetoxy-2-(5-dimethylhydrazonofur-2-yl)-1,4-naphthoquinone (11) formed purple irregular prisms which change shape upon heating between 150 and 155 °C and melt at 165–167 °C (67%): hexane/CH_2Cl_2; IR (KBr) 1760 ($\nu_{C=O}$), 1665 ($\nu_{C=O}$), 1635 ($\nu_{C=O}$) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.06 (dd, 1, $J_{5,6}$ = 7.62 Hz, $J_{6,7}$ = 7.62 Hz, H_6), 7.63 (dd, 1, $J_{7,6}$ = 7.62 Hz, $J_{7,5}$ = 1.20 Hz, H_7), 7.33 (d, 1, $J_{3',4'}$ = 3.82 Hz, $H_{3'}$ or $H_{4'}$), 7.31 (s, 1, H_3), 7.03 (s, 1, *H*C=N), 6.59 (d, 1, $J_{3',4'}$ = 3.82 Hz, $H_{3'}$ or $H_{4'}$), 3.09 [s, 6, $N(CH_3)_2$], 2.48 (s, 3, CH_3); MS, $M^{\bullet+}$ 352 (10), 258 (11), 174 (100), 119 (42).

Anal. Calcd for $C_{19}H_{16}N_2O_5$: C, 64.77; H, 4.58; N, 7.95. Found: C, 64.81; H, 4.62; N, 7.94.

2-Acetylfuran Dimethylhydrazone. To 2-acetylfuran (30.0 g, 0.27 mol) in benzene (20 mL) containing TsOH (100 mg) was added *N,N*-dimethylhydrazine (16.4 g, 0.27 mol) slowly. The solution was brought to reflux and water formed in the reaction was removed in a Dean–Stark trap. After 5 h benzene and excess hydrazine were removed under reduced pressure. The remaining solution was distilled through a Virgeux column affording the hydrazone as a yellow oil: 24.3 g (70%), bp 34–40 °C/0.1 mm; ^1H NMR (200 MHz, $CDCl_3$) δ 7.48 (d, 1, $J_{4,3}$ = 1.72 Hz, H_4), 6.68 (d, 1, $J_{2,3}$ = 3.41 Hz, H_2), 6.44 (dd, 1, $J_{3,4}$ = 1.72 Hz, $J_{3,2}$ = 3.41 Hz, H_3), 2.61 [s, 3, $N(CH_3)_2$], 2.27 (s, 3, CH_3).

5-Nitrofurfural Dimethylhydrazone. To 5-nitrofurfural (25.0 g, 0.18 mol) in benzene (20 mL) containing TsOH (100 mg) was added *N,N*-dimethylhydrazine (11.0 g, 0.18 mol) slowly. A bright red solid immediately began to precipitate. The mixture was refluxed for 4 h and water formed in the reaction was removed in a Dean–Stark trap. The mixture was cooled to room temperature and filtered. The solid was dissolved in $CHCl_3$ and treated with decolorizing charcoal. Evaporation of the $CHCl_3$ afforded the hydrazone as bright red prisms: 26.3 g (80%), mp 110–111 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 7.33 (d, 1, $J_{3,4}$ = 8.0 Hz, Ar), 6.90 (s, 1, *H*C=N), 6.58 (d, 1, $J_{3,4}$ = 8.0 Hz, Ar), 3.13 [s, 6, $N(CH_3)_2$].